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THE REMOVAL OF COLOR FROM TNT WASTE

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THE REMOVAL OF COLOR FROM TNT WASTE[1]

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SYNOPSIS

Research on the removal of color from TNT wastes was conducted at New York University College of Engineering in the Lewis Van Carpenter Sanitary Engineering Laboratory. Laboratory and field station results obtained with chlorination are discussed. Other less successful methods of treatment are mentioned. The efficiency of sellite waste color removal with chlorine is demonstrated.

INTRODUCTION

Disposal of sellite waste presents a problem of considerable magnitude. Persistent color characteristics make it objectionable in high dilutions. The taste is accentuated by small quantities of chlorine applied in water treatment application. Leaching of color-containing, soluble solids into ground waters practically eliminates land as a disposal medium. Disposal by evaporation is costly and the syrup concentrate remaining after evaporation offers additional difficulty.

Accordingly, the Office of the Surgeon General, U. S. Army, and the Research Division, New York University College of Engineering have cooperated in research on Sellite Waste Water Treatment with the objective of finding, if possible, a method or methods of removing color.

The Waste

Commercial symmetrical trinitrotoluene is formed by the nitration of toluene under controlled conditions. Small amounts of the unsymmetrical isomers are produced and it is necessary to remove these side products because of undesirable properties such as instability. Pure symmetrical trinitrotoluene can be separated from the undesirable compounds by making use of the difference in solubility in sodium sulfite solution. Commercially important trinitrotoluene or TNT is almost completely insoluble in this sulfite or sellite solution whereas the unsymmetrical forms and other impurities are almost completely soluble.

Waste sellite liquor or TNT red water is very highly colored, has a very bitter taste and is toxic. It contains a high concentration of dissolved solids much of which is inorganic salt. The waste is generally slightly alkaline with

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a pH of about 8.1, free from turbidity and reddish brown in color. The dissolved solids vary from about 7 to 10 percent.

A careful study of the amount and nature of the waste made by the Army Environmental Health Laboratory and New York University in 1953 indicated that the average waste volume was 1.11 ± 0.10 gallons per pound of TNT produced and the average color was 229,000 ± 49,000 as measured by platinum cobalt standards. The color of the waste increases on standing and becomes more difficult to remove.

Laboratory Studies

Although considerable work has been done on the removal of color from TNT red water, the results generally have been unsatisfactory. The color has been very resistant to biological and chemical attack. Preliminary studies indicated that reducing substances such as sulfur dioxide, sodium thiosulfate, ferrous sulfate and hydrosulfides are not effective. Adsorption on materials such as clays and activated carbon may remove much color, but is impractical because of cost. All of the color can be removed by ion exchange, but short cycles and difficulty in regeneration seem to make this method uneconomical.

Oxidizing agents seemed to show the most promise of success and several including chlorine, chlorine dioxide, bromine, sodium peroxide and ozone were tried. Only chlorine removed color at a reasonable cost.

The first studies were made on wastes shipped to New York University. They varied widely in strength. The color increased on standing and became increasingly difficult to treat.

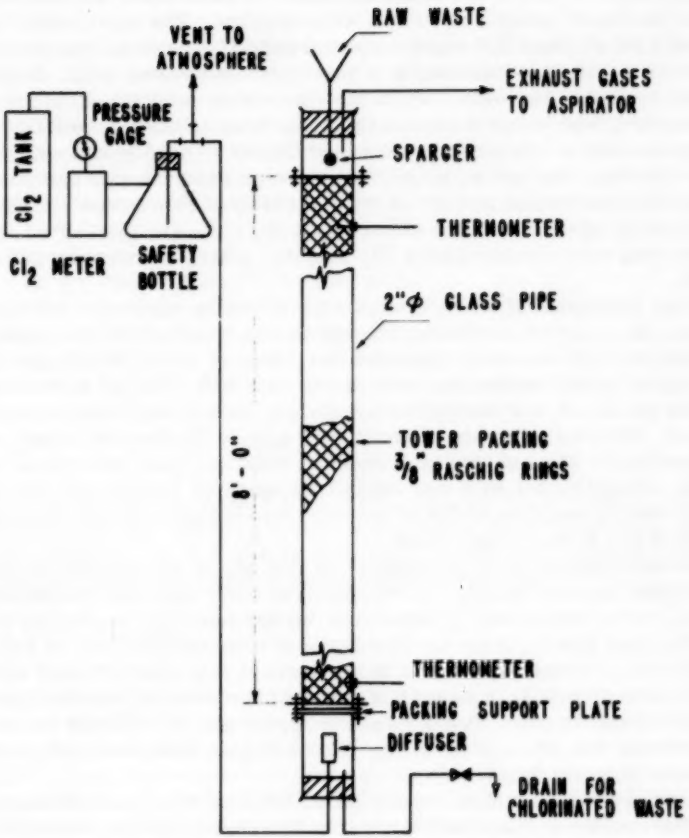
Chlorination with Hypochlorite

Experiments with calcium hypochlorite indicated that a high percentage of the color could be removed, depending upon the original color and the chlorine dosage. With low color values in the order of 5600, all of the color was removed with 2200 ppm of chlorine and the color did not return on standing or when the solution was made alkaline.

With high color values in the range of 180,000-200,000, the color could be reduced to about 1500 with 70,000 to 100,000 ppm of chlorine. The reaction took place rapidly with foaming, increase in temperature and formation of a precipitate which varied with the amount of calcium hypochlorite added. The pH was lowered some, depending upon the chlorine dosage. The large amount of lime added with the chlorine neutralized much of the hydrochloric acid formed in the chlorine reaction. The residual chlorine varied from 350 to 2200 ppm after two minutes of contact, and from 100 to 1400 ppm after ten minutes. The color increased when the solution was allowed to stand or when it was made alkaline. The color remaining after chlorination is a yellow similar to that found in natural waters and could be mixed with natural waters with little complaint about color.

Chlorination with Chlorine Gas

In order to study the effect of gaseous chlorine on the waste, a pyrex glass tower, two inches in diameter and ten feet long, was set up. It was packed with 3/8 inch Raschig rings to provide thorough mixing of gas and liquid and to furnish a large surface upon which the reactions take place. Measured amounts of chlorine gas entered the bottom of the tower through a diffuser,



CHLORINATION TOWER

FIGURE 1

and, in continuous operation, the waste entered the top of the tower and was sprayed over the packing by a sparger. Exhaust gases were drawn off at the top by an aspirator and discharged after passing through a solution of caustic soda. The essential parts of the tower are shown in Figure 1. The chlorine feed was controlled by a Wallace & Tiernan volumetric direct feed chlorinator.

In batch chlorination of the waste (color 125,000), about 15,000-25,000 ppm of chlorine were required to reduce the color to about 8,000 and foaming began when the liquid became saturated with chlorine. The chlorinated liquor which had a pH of about 1.0 was yellow and turbid. The main reaction took place very quickly, but continued at a slow rate for several days. On standing, the colors tended to increase. When the liquor was neutralized, some of the color returned, which indicated that the color is an indicator, reddish and strong in alkaline solutions and yellow and lighter in acid solutions. It was evident, however, that the major portion of color removal with chlorine is the result of chlorination and not strictly a result of pH change. Acidification with sulfuric acid effected only 45% removal after the samples stood several days, whereas color removal with Cl_2 was immediate and usually was greater than 90%.

Chlorine treatment of waste diluted with tap water seemed to be more satisfactory. On a continuous basis, chlorination of waste which had been diluted with three parts of tap water indicated that doses of about 30,000 ppm (based on raw waste) would reduce the color more than 90%. The pH of the treated waste was about 1.0, but neutralization did not seem to increase the color a great deal. Residual chlorine of about 1500 ppm in the treated liquor seemed to be necessary. Most of this high residual chlorine could be utilized by diluting the treated liquor with raw waste. As much as 4 to 10 percent of raw waste by volume could be added to the chlorinated waste without increasing the color of the mixture very much.

It seemed impractical to chlorinate the raw waste, as received in New York, without dilution because of the return of color upon neutralization and, therefore, tests were made to determine the optimum dilution before chlorination. The best result, from the standpoint of chlorine dose and of residual color after neutralization, seemed to be obtained with waste diluted with two or three parts of water. A sample of red water, stored for several months and very difficult to treat, required about 30,000 ppm of chlorine to reduce the color from 240,000 to about 3500. These values have been computed back to 100 percent waste basis.

Samples of relatively fresh waste (color 200,000) were somewhat easier to treat. The results of chlorination experiments indicated that with a dilution with three parts of water, an average of 22,200 ppm chlorine based on undiluted waste was required and with two parts of water, an average of 26,300 ppm of chlorine was required.

During the laboratory studies, it was discovered that if the pH of the chlorinated waste was adjusted to neutrality as soon as possible after chlorination, the color return was much less than if the chlorinated waste was allowed to stand several hours before neutralization. For example, in one test, the color of the treated waste (based on 100 percent waste) was 18,000. The pH was immediately adjusted to 6.0 and the color increased to 27,000. On standing overnight, the pH dropped to 4.2 and the color increased to 33,000. The pH was adjusted again to 8.0 and the color increased to 36,000, giving a net overall removal of 85 percent. When a sample of this same chlorinated waste was permitted to stand for four hours before neutralization to pH 6.0,

the color increased to 42,000. On standing overnight, the pH dropped to 5.5 and the color increased to 52,500, a reduction of only 78 percent.

Field Studies

Since the wastes increased in color and in difficulty of handling with age and since they were usually several weeks old when received at New York University, it seemed desirable to make similar tests in the field on fresh waste.

A glass tower 17 feet high and two inches in diameter was installed at a TNT plant to treat fresh wastes. The column was fitted on the bottom with a ceramic chlorine diffuser and a drain for removing the treated waste. At the top of the column was a constant feed tank for the addition of red water and a vacuum line to a water aspirator to remove any excess chlorine and the gases generated during the operation. The first tests were made without any packing material in the column. Later the tower was packed to a height of 15 feet with Raschig rings, 3/8 x 3/8 inches and the packing was supported by a lucite plate. A Wallace and Tiernan direct gas feed chlorinator was used to measure the amount of chlorine used.

In operation, the column was filled with red water and chlorine was fed into the bottom of the column. When the color change reached a predetermined height, usually five feet from the bottom, the waste was fed into the top at a constant rate and the treated material was withdrawn from the bottom. The constant color level was controlled by the chlorine dose.

Results

Six sets of data were obtained with the column not packed and ten sets were obtained with the column packed. All of these tests were made with the column flooded, i.e., full of liquid, except one, which was made with a continuous gas phase and liquid trickling over the packing.

Column Without Packing

In some types of chlorination, excellent results have been obtained in a column of liquid without packing material. Six sets of data were collected using various dilutions of waste in the column before the packing material was added. Previous data obtained at New York University had indicated that dilution of the waste was necessary to prevent return of color after neutralization of acidity. The data shown in Table 1 indicate that chlorine dosages of 10,000 to 16,000 ppm (based on color of raw waste) were needed for 86-99% removal of color. The stronger the color, the greater was the efficiency of color removal. As the waste was diluted, more chlorine was required. These results were far better than those obtained with wastes shipped to the New York University Laboratory and indicated that the fresh waste required only about one half as much chlorine as was needed by the older waste for comparable color removal.

Column With Packing

After the column was packed with Raschig rings, ten sets of data were obtained using undiluted waste and various dilutions made with flaker-condenser water. All experiments except No. 12 were made with a flooded column. In Experiment 12, the liquid trickled over the packing material as the chlorine passed up through it. The change of color level was maintained at 1.5 feet

Table 1

FIELD STUDIES - TNT WASTE

Color Removal with Chlorination
in
Packed and Unpacked Tower

Exp. No.	Dilution	Color In	Cl_2 Raw Basis	ppm Cl_2 Unit Color	Efficiency of Color Removal	Color of Neutralized Treated Waste	
						at pH	Value
Without Packing							
2	3:1	45,000	15,500	.0886	95.5%	7.9	2,000
3	3:1	50,000	13,440	.0673	95.0%	7.1	2,500
4	2:1	50,000	12,600	.084	90.0%	7.0	4,000
5	2:1	50,000	13,600	.0908	92.0%	7.1	3,000
6	4:1	30,000	16,800	.112	86.6%	7.2	3,000
7	1:1	100,000	10,000	.05	97 %	7.4	4,000
With Packing							
8	no dilution	150,000	7,930	.0528	98.6%	7.5	4,000
9	no dilution	200,000	8,800	.044	98 %	8.6	10,000
10	1:1	100,000	9,740	.0487	98 %	7.6	3,000
11	2:1	25,000	15,120	.15120	94 %	7.5	2,000
12	2:1	50,000	15,120	.0756	97 %	6.1	7,000
13	2:1	50,000	16,650	.08325	97 %	7.1	3,000

from the bottom of the column. With the raw waste (color 200,000) diluted with two parts of water, the chlorine dosage based on the raw waste was 15,120 ppm and the color of the treated waste 6000, based on raw waste. After neutralization, the color increased to 21,000.

The data on the packed tower (Table 1) show that 8,000-16,500 ppm chlorine were needed depending upon the dilution. Two samples of raw undiluted waste required about 8400 ppm of chlorine to reduce the color from about 175,000 to about 7000. A third undiluted sample required only 4200 ppm of chlorine, but the color reduction was relatively poor and much of the color returned after the acidity was neutralized. Three samples diluted with two volumes of water required more than 15,000 ppm of chlorine. The units of color removed per part per million of chlorine added, plotted against the initial color of the sample added to the column, are shown in Figure 2. The greater the dilution and therefore the lower the color in the waste added to the column, the poorer the efficiency in removing color. For example, only 6.2 units of color were removed per part per million of chlorine when the initial color was 25,000, but 22 units were removed with an initial color of 200,000. It is apparent that chlorination of the raw material without dilution is efficient from many standpoints.

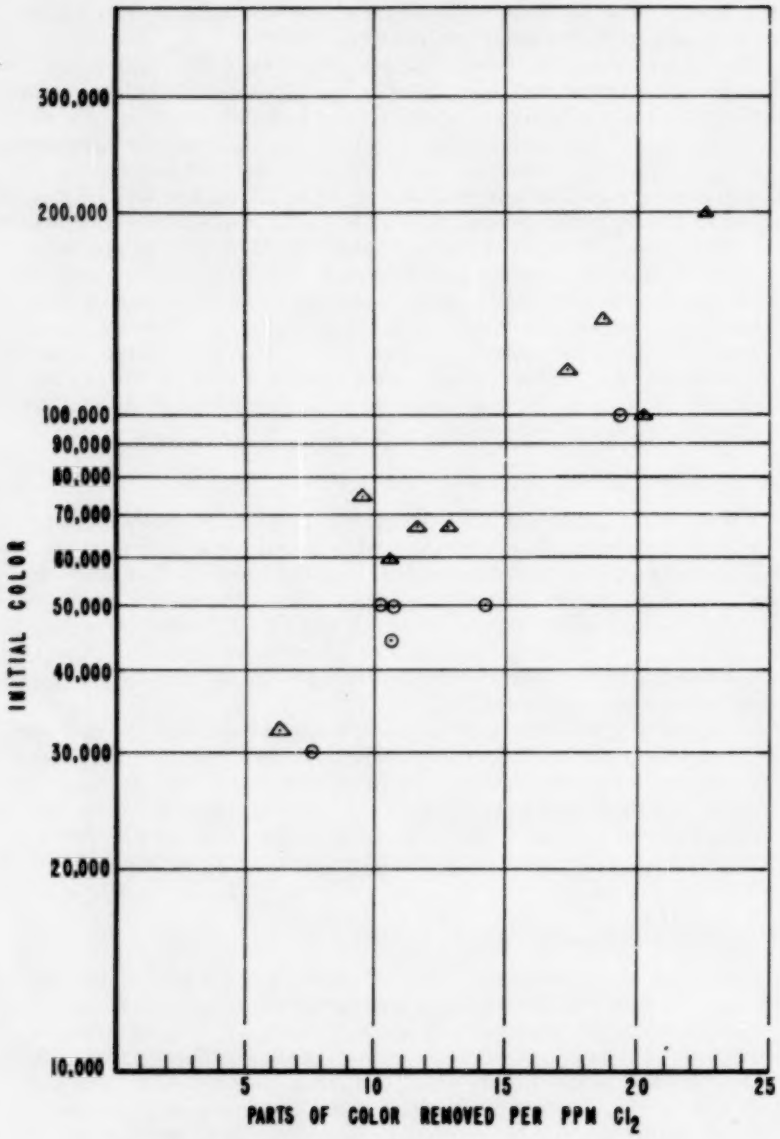
Effect of Neutralization of Acidity

Since the chlorinated wastes are always acid and since they must be neutralized before discharge to a stream, sodium hydroxide was added to the samples as the effluent was discharged from the column. The effect on color was not constant. In half the samples, the colors increased on neutralization of the acidity. In most cases the increase was small. In the other half of the samples, the color remained the same or decreased slightly. No relationship between the change in color and the amount of residual chlorine or the dilution of the sample is observed.

The neutralized samples were allowed to stand overnight or, in a few cases, over the week-end. The pH always decreased on standing. About half of the samples increased in color and about half decreased. Complete immediate neutralization of the acid does not seem necessary. Some data indicate that if enough caustic is added to the waste to bring the pH up to about 3.0 immediately, more caustic can be added an hour or so later without the return of color.

Neutralization of Residual Excess Chlorine with Raw Waste

Chlorinated waste containing residual chlorine has a potential color reducing power. In order to demonstrate whether or not the residual chlorine could be used, the pH was neutralized and mixtures of 5 ml of raw waste with 95 ml of neutralized chlorinated waste were made up. Since most of the samples were diluted before chlorination, the actual percentage of raw waste added, in terms of original raw waste present in the sample, varied from 5 to 30 percent. In general the overall reductions in color were good, averaging about 85 percent. The results showed that the chlorine dosage can be further reduced by the addition of raw waste to the chlorinated sample. As a general rule, based on the color of the sample immediately after mixing, raw waste, equivalent to 20% of the waste in the chlorinated sample, can be added without increasing the color. Based on the samples which were stored 24 hours after mixing, raw waste equivalent to about 10% of the waste in the chlorinated sample can be added without increasing the color. Since, in most



RATIO – PARTS COLOR REMOVED PER PPM Cl_2 ADDED VS INFLUENT COLOR

FIGURE 2

cases, the immediate color is most important, the chlorine dosage is effectively reduced from 9000 ppm to 7200 ppm.

SUMMARY

Fresh TNT sellite waste can be chlorinated directly in a column and more than 90% of the color can be removed with about 9000 ppm of chlorine.

The acidity formed by liberation of hydrochloric acid can be neutralized automatically at the column without return of color.

The residual color in the chlorinated waste is a yellow, similar to that found in natural waters and is much less objectionable than that of the raw waste.

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